

Rapid Feedstock Characterization

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Abstract

Rapid Feedstock Characterization using near infrared spectrometry. Aimee Ginley
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To make corn stover into ethanol constituent values must first be known. Previously this was done through a wet chemistry method that cost around a thousand dollars and took about a week to perform. The method currently being explored costs only around ten dollars and takes less than ten minutes to analyze the same amount of corn stover. To get an accurate reading of the constituents in the total 32m³ feedstock sample, the sample was broken up into smaller and smaller samples, then analyzed at the smallest level. Then the individual results were averaged to gain information about the feedstock sample as a whole. The corn stover samples turned out to only be homogenous within a range of about two weight percent for the feedstock sample. This meant that the one bag, wet chemistry method being used previously did not give accurate readings because it is impossible to know where in the range the bag sampled lies.

Research Category (Please Circle)

ERULF: Physics Chemistry Biology Engineering Computer Science Other _____
CCI: Biotechnology Environmental Science Computing

TYPE ALL INFORMATION CORRECTLY AND COMPLETELY

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Introduction

Different types of biomass can are being investigated at NREL as potential feedstocks for the production of ethanol, which, in the future, could be an important, and economic fuel source and replacement for fossil fuels. Ethanol is produced by fermenting sugars, in a process similar to that, which is used to make beer. These sugars can be found in a variety of sources including waste biomass. Ethanol can be used as a fuel in its pure form or blended with gasoline to help reduce the emission of carbon monoxide and hydrocarbons from vehicles. Currently it is used as an additive to fuel on high pollution days (NREL,1998) Corn stover, the portion of the plant that is left after the ear of the corn has been harvested, is being explored at NREL as a possible biomass feedstock for this process. In order to understand and optimize the process used in ethanol production, the chemical composition of the feedstock must be known.

Historically, the Ethanol Process Development (EPD) team at NREL has sent out their corn stover samples for commercial analysis to get information about the chemical constituents critical for ethanol production. An average value for the feedstock was then used to evaluate the processes used for ethanol production. One problem with this procedure is that it assumes that one small sample can fully represent the chemical composition of corn stover used in large scale ethanol production. The traditional wet chemical methods also have other limitations that prohibit their application in commercial processes. A complete wet chemical analysis costs about \$1,000 per sample, includes more than twenty individual procedures and takes at least a week to perform. This long delay in getting data and the cost of the procedure prohibit the acquisition of enough data for the ethanol process development effort.

Bonnie Hames and the Rapid Analysis team at NREL have been working on the analysis of feedstock using Near Infrared (NIR) spectroscopy, so they were asked to help out with the Ethanol Program's analysis of their most recent corn stover feedstock. The NIR method provides several advantages when compared to the wet chemistry method. The NIR method takes only ten minutes and costs less than ten dollars to produce a comparable composition analysis of a sample of corn stover. The NIR method also requires almost no sample preparation. With the lower costs and reduced analysis time, the Ethanol program would not only save money, but could use the additional levels of information to help achieve the goal of optimizing the ethanol production process. Specifically they could analyze a wider number of samples from a batch of corn stover and for the same cost, have more information about the ethanol production process.

Materials and Methods

Chemical data was collected on the corn stover using reflectance spectroscopy in the near infrared and visible regions of the electromagnetic spectrum. The Infrared (IR) spectrum can be divided into three regions; Far IR from 5,000 to 100,000 nm the mid IR region from 2,500 to 5,000 nm, and the near IR region from 800 to 2500 nm- The near infrared region is used because this is the region where organic chemical bonds CH, NH, OH, and CO are seen. (Shenk, 2000) These types of bonds are found in the chemical structure of glucan, xylan, and lignin, the basic constituents in which the Ethanol team is interested. The instrument used was a Foss 6500 visible/NIR forage analyzer that scans the region of 400 to 1250 nm. (Photo 1) There are three basic ways to make a NIR spectroscopic measurement. They are reflectance, transmission, and folded transmission. Reflectance, the measurement we make with our eyes, is a measurement of the infrared

that is essentially bounced off of the sample. This type of measurement is made with both the source and the detector on the same type of the sample. Making the measurement with transmission means that the detector is on the other side of the material and the detectors are on the opposite side of the material than the light source. Folded transmission is used for clear liquids, where the radiation passes through the liquid, hits a reflecting surface, and is reflected through the material again where it hits a detector. The near infrared spectrometer we used measured the reflectance spectrum that was collected after the sample has absorbed some of the infrared wavelengths. Absorption occurs when energy is emitted from the source (a light bulb) at a frequency that corresponds with the vibration of a bond and the energy is absorbed by the bond. (Shenk, 2000) There are two types of vibrations, stretching and bending. A stretching vibration is a rhythmical movement along the bond axis. This causes the distance between the atoms to increase or decrease. A bending vibration may consist of a change in bond angle between bonds with a common atom. Bending may also occur because of the movement of a group of atoms with respect to the remainder of the molecule. Only the vibrations that result in a rhythmical change in the dipole moment of the molecule are observed. (Silverstein and Webster, 1998) The NIR analyzer was designed for use mainly with forage and animal feeds, because of this the system is able to handle both small milled and large coarse samples. The NIR spectrometer was equipped with a transport module, which moves the sample up and down during data collection. For each sample a total of 33 spectra were collected and averaged to fully take into account the heterogeneity of the sample. The biomass sample was placed in a Foss Natural Products cell to be analyzed. The cell, a deep rectangular container, is large enough to

accommodate handful-sized samples of coarsely chopped material. The cell also has a window made of clear quartz to avoid interfering with the spectroscopy, because window glass has a signal in the NIR region and quartz is invisible in the NIR region (Roberts and Caserio, 1967). (Photo 2)

The information contained in a NIR spectrum is not obvious to the naked eye. When the raw spectroscopic data is examined, only general trends can be identified in terms of what organic bonds are present. To extract the compositional information from the spectroscopic data, a comparison is made to the NIR spectra of a set of calibration samples with known composition. For this experiment the calibration set consisted of approximately sixty samples of corn stover from the same location as the samples to be analyzed. To make the calibration equation that converts the spectroscopic data into the chemical data a powerful computer program is used. The program solves matrices of hundreds of equations and thousands of variables using the partial least squares (PLS), or projection to latent structures, method. This method projects the constituent matrix into the NIR matrix to make an equation that relates spectroscopic changes to changes in the concentration of the constituents. This equation is used each time samples of corn stover are analyzed and calculates the weight percent of the calibration constituents. Because the whole equation is based on it, the most important part of the calibration process is starting with carefully analyzed calibration samples. (Shenk, 2000) Two sources of error must be considered at this point. They are how accurate, and how repeatable the method is. Accuracy is the agreement between the calibration value and the predicted value, and repeatability is the agreement among subsamples of the same material, or subsamples analyzed by different instruments.

Confounding the issue of feedstock compositional variation was the problem of soil contamination. In earlier experiments unwashed corn stover was used as a process feedstock. A recent feedstock storage study demonstrated that the corn stover feedstock could contain as much as 30% dirt when it was used unwashed. The dirt could cause process problems because even if it was found that the corn stover chemistry did not vary, the dirt chemistry was an unknown variable that could easily change. Also, the dirt could have been composed partially of fertilizer, and the fertilizer's components could affect the ethanol production reactions enough to change the price. In an effort to solve this problem the Ethanol program decided to wash the corn stover before putting it in the reactor. Washing the stover prior to NIR analysis meant that the samples for compositional analysis were as much as 80% water when delivered to the rapid analysis team.

Since the PLS method was calibrated using dry corn stover samples, the rapid analysis team had to dry the corn stover prior to NIR spectroscopy. The stover was either dried by letting it air dry naturally over several days, or by placing it in a no heat convection oven. (Photo 3) Usually the corn stover, which was delivered at as much as 85% moisture, was air-dried over night and then transferred to the convection oven for more rapid drying. The samples were removed from the oven after intervals of one to two hours for moisture determination and spectroscopic analysis. Using this procedure, the changes in the NIR spectra could be tracked as a function of decreasing moisture content.

My experiment was designed to determine the level of homogeneity within the bulk feedstock. To do this, the feedstock to be examined was broken down into many

different levels. The bulk feedstock consisted of 32 one meter cubed totes. Five to ten one-half gallon bags of stover were collected from each tote. These bags were then delivered to the Rapid Analysis team. Each bag was further broken down into four handful-size samples. Near Infrared spectra were collected on each of the handful-sized samples. After the handful-sized samples were analyzed the data was averaged at the bag, tote, and feedstock levels.

Results

When the corn stover samples were wet, the equation predicted lignin contents that were very low, sometimes even negative,. The sugar, glucan and xylan, predictions were also seen to be unusually high in the wet corn stover. As the samples dried, the lignin numbers increased and the sugar numbers decreased until the moisture level in the corn stover reached approximately ten percent. (Figure 1) At around ten percent moisture the changes in predicted concentration of the constituents leveled out and the predicted values for the important constituents fell within normal values for corn stover. At about ten percent moisture the NIR spectra were similar enough to the calibration set that an accurate prediction could be made using the calibration equation. The total mass closure numbers increased from around seventy percent up to the high eighties to mid nineties, matching the mass closures of the calibration data. The interference of water with the PLS prediction became apparent when the spectra of wet and dry samples were compared. When the sample of corn stover, was wet, only large OH bond peaks could be seen in the NIR spectrum. As the corn stover dried these peaks receded and left a spectrum rich in information about the chemical composition of the corn stover. (Figure 2)

The WinISI software package that the Rapid analysis team uses reports a Global H value with each prediction. The Global H value (Mahalanobis distance) represents the distance from the center of the calibration spectrum in multidimensional space (WinISI 2000). This number gives the operator a way to determine the appropriateness of the calibration set for the analysis of each sample. A global H value of 3 or less indicates that the sample is part of the same population as the calibration set, a condition necessary for a robust analysis. As the samples approached the ten percent moisture level, global H values fell below 3.

Discussion and Conclusion

It was found that the wet corn stover could not be analyzed using the current PLS calibration equation. The OH peaks of the water obscure the spectroscopic features that contain the lignin and sugar information to a point where the equation is unable to produce correct data. Only drying the samples to moisture levels below ten percent allowed the collection of quality NIR spectra, which could be used for rapid compositional analysis. This presented a problem because it added a time consuming, and labor intensive step to the process of analyzing the corn stover. Currently the Rapid Analysis and EPD teams are working on developing a way to analyze the corn stover, and remove the dirt in a more time efficient manner. They are beginning to experiment with mulching the corn stover, to remove the dirt without wetting the samples. If this works, the stover will be harvested at a moisture level appropriate for rapid analysis. This might make it possible to start analyzing the corn stover in real time as it goes into the reactor.

When the corn stover was analyzed at the handful level, each handful could be distinguished by slight chemical difference in the constituents. (Figure 3) However,

when the compositions of the handfuls were averaged at the bag level, almost no difference could be seen in the chemistry of the different bags. (Figure 4) Minor differences between totes were observed when the bag-level information was averaged. With this information, the composition of the corn stover feedstock could be more accurately reported as a range of values rather than an exact number. (Figure 5) Realistic information about possible variation in feedstock composition will be used to develop ethanol production processes that are robust enough to accommodate this variation with minimal impact on ethanol production cost.

After the corn stover was analyzed the variance in the chemical composition of the bulk feedstock could be determined. The constituents of the totes varied as shown in table X. . This variance could be significant to the economics of ethanol production from corn stover. The infrared spectrometry can give the EPD team an accurate assessment of the average chemical composition of their feedstock as well as the expected normal variance in those values. The chemical analysis performed during this internship would have cost \$450,000 if performed by a commercial laboratory and would have taken approximately 45 weeks. Rapid analysis enabled this evaluation to be performed in 9 weeks for \$4,500 by an inexperienced intern.

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Foss 6500 Visible/NIR Forage Analyzer



Photo 2
Natural Products Cell



Drying racks used for air drying
Figure 1

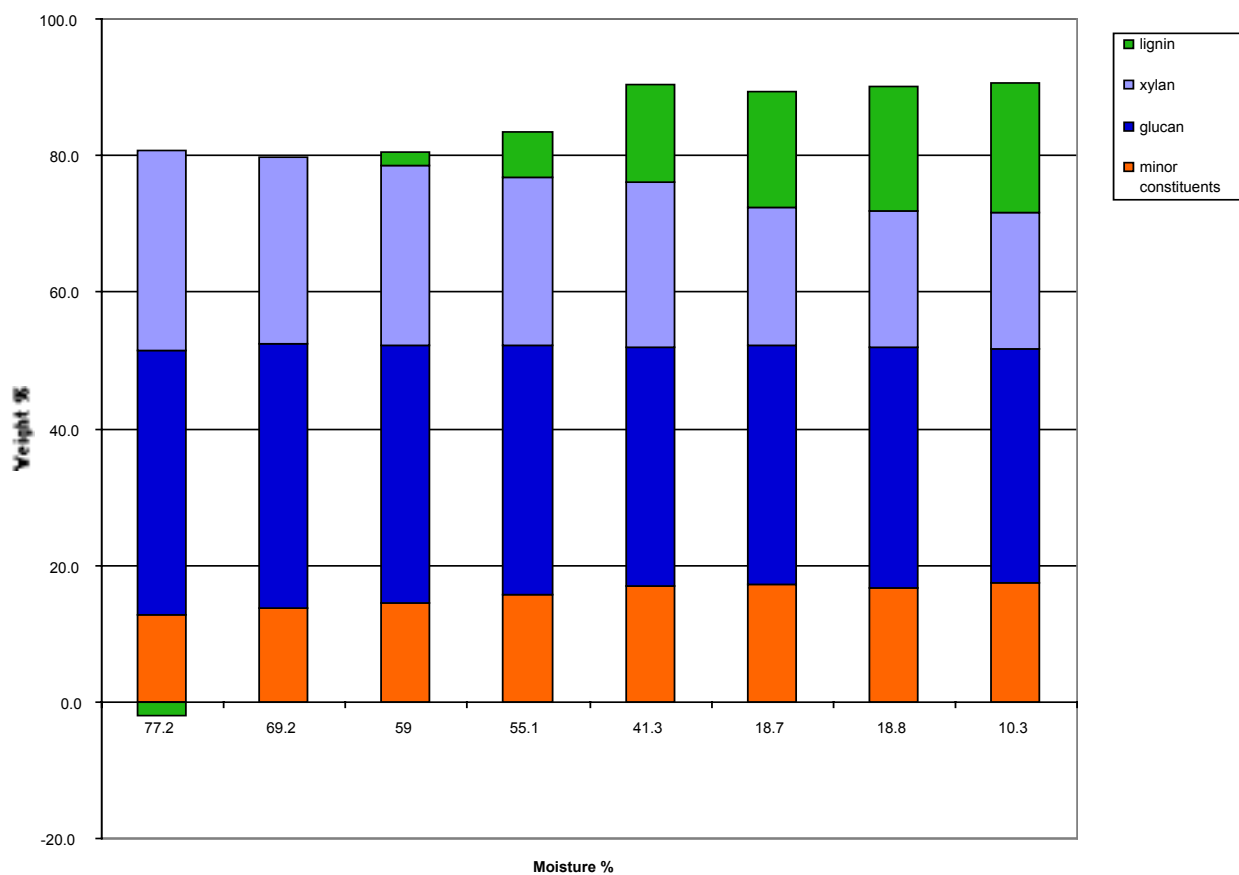


Figure 1
Graph of Bag drying

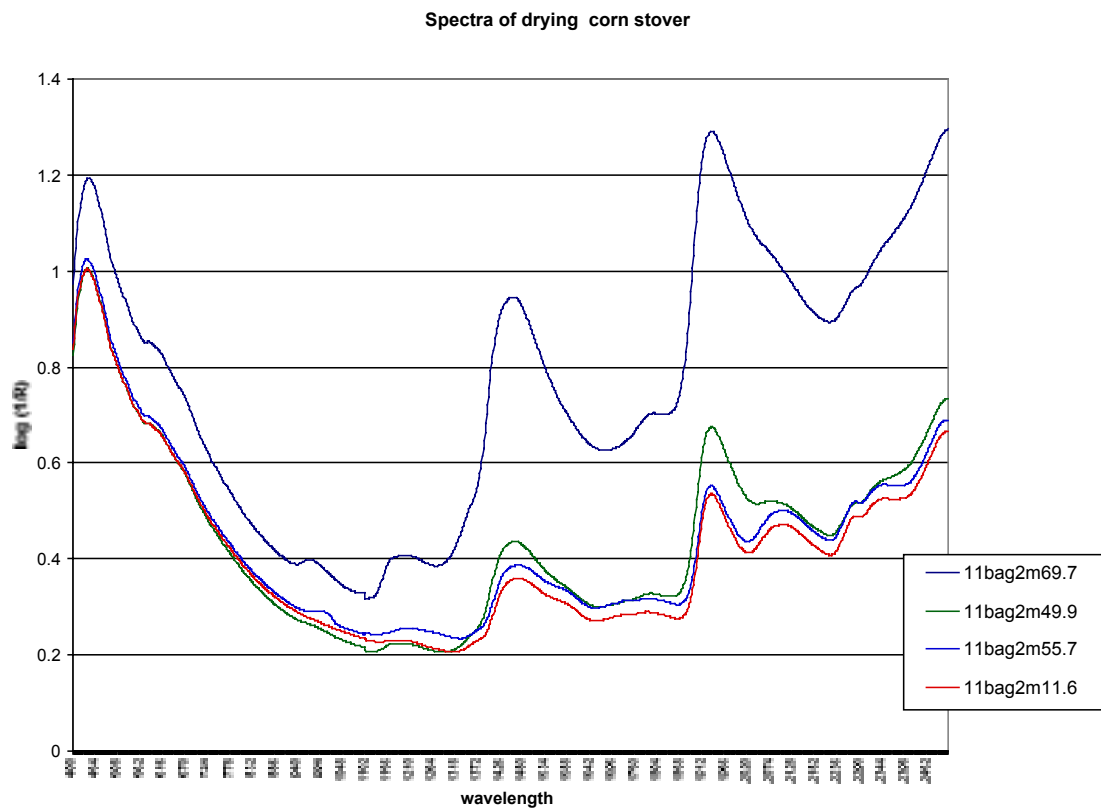


Figure 2
Graph of spectra as bag dries

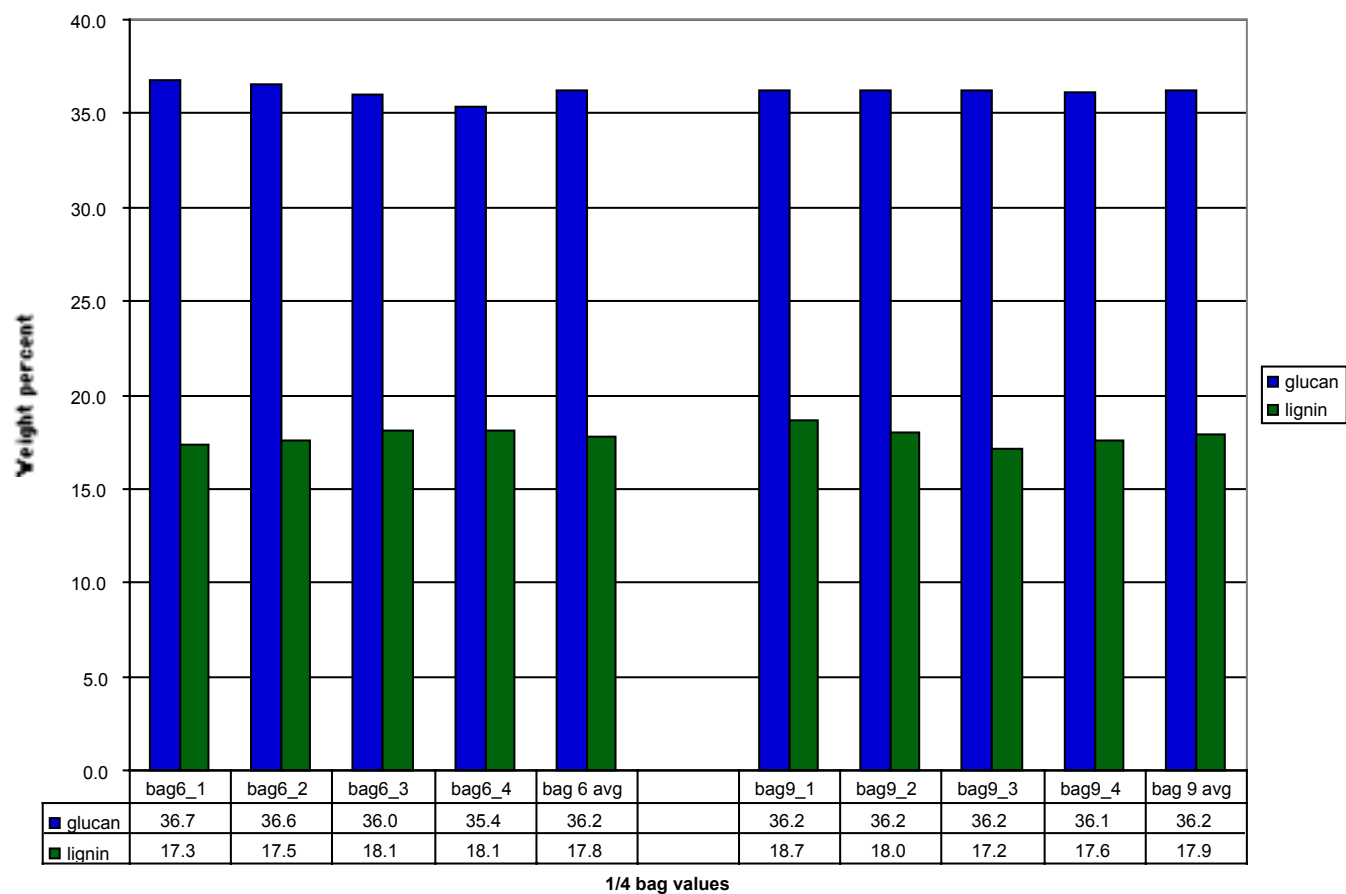


Figure 3
Graph of two bags from the same tote

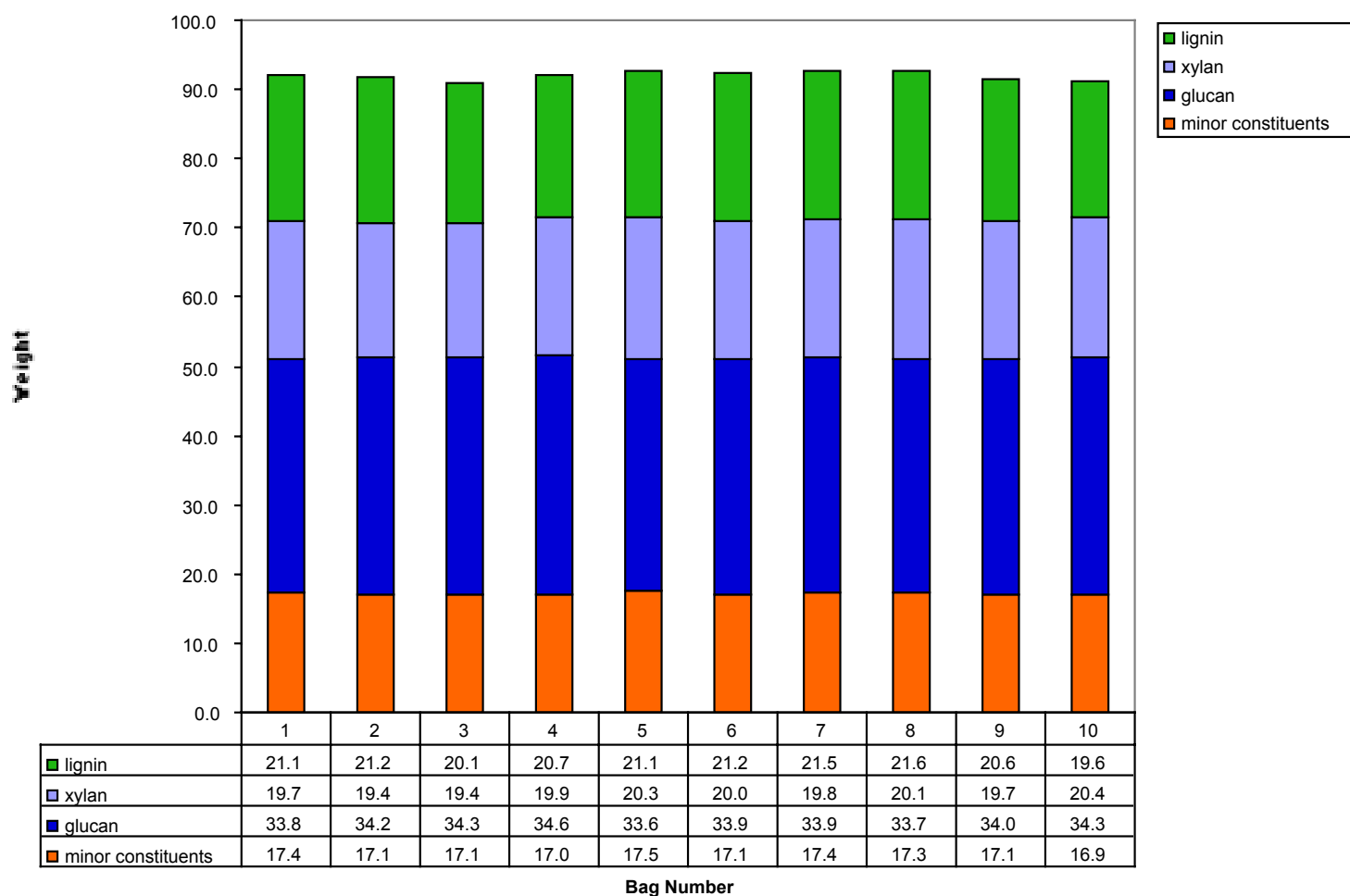


Figure 4
Graph of Averaged Bags in Tote

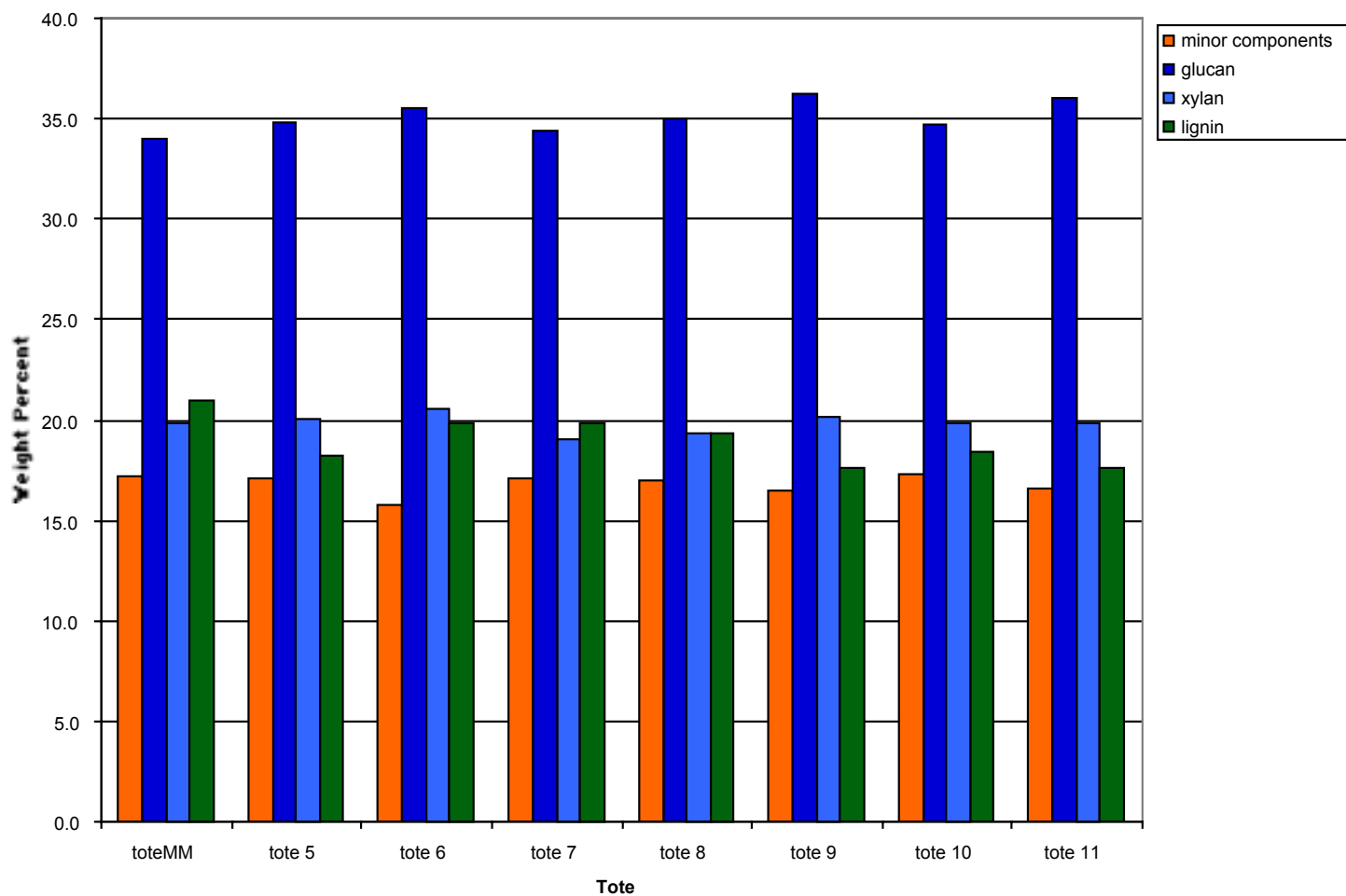


Figure 5
Graph of averaged totes